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A Sensor for Water Detection in Aircraft Adhesive Bondlines

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ABSTRACT

A simple and low cost sensor for detecting the water ingress in the adhesive bond line was designed. A compressed polypyrrole (PPy) powder was embedded in an epoxy adhesive sandwiched between two aluminium (2024) substrates. Interactions between PPy and water resulted in a rapid increase in resistivity. The DC resistivity increased more than 20 times the initial value when the PPy was contacted by water. The increase was consistent with AC impedance at low frequencies which showed 10 times increase if one PPy disc (3 mm diameter) was embedded or 100 times increase if there were 3 PPy disc embedded when the cell was immersed in a brine solution for approximately 1000 h. The resistivity of compressed PPy embedded in the bondline was unchanged after 2000 h ageing at 100 C. This indicates a good thermal stability. An initial test indicated that the inclusion of a single 5mm diameter PPy disc in a 25mm diameter bonded joint did not significantly decrease the dry adhesive strength of the adhesive joint. These results indicate that the sensor could potentially meet the requirements of a bond degradation sensor in terms of (1) low cost (few cents for one PPy disc) (2) sensitivity to water (3) long-term stability (4) ease of monitoring and (5) sustaining the dry bond strength.

RELEASE LIMITATION

Approved for public release

A Sensor for Water Detection in Aircraft Adhesive Bondlines

Executive Summary

Australian military aircraft such as the F/A-18 and F-111 have adhesively bonded structural components. Water ingress leading to debonding of structural components is an issue of importance to the structural integrity of these aircraft. Sensors capable of detecting low level of water ingress into an adhesive bondline are being developed as a device to assist with the maintenance of bonded components in RAAF aircraft. Water ingress into a bond line is also a precursor to corrosion damage of the aluminium substrate and stiffening members in bonded sandwich panel structures. Therefore, early detection of water in the bondline is an important factor in monitoring the health of an aircraft. In this study, an electroactive polymer, i.e. polypyrrole (PPy) powder, was exmined as a water detecting material when embedded in aluminium /adhesive joints and in contact with the aluminium substrate. It has been found that when PPy is in contact with a trace of water, both the DC and AC resistivity increases rapidly. The sensitivity of the sensor depends strongly on the number of PPy discs used in the cell stack. With a three disc stack the sensitivity for a water saturated joint can increase by 100 times the initial dry value. In practical terms, the DC resistivity changes is readily monitored using a multimeter.

This study indicates that PPy meets the principal requirements of a bond degradation sensor in terms of (1) low cost; (2) simple operating principle; (3) simple manufacturing method; (4) long-term stability in an airless environment; (5) sustaining dry adhesive strength and (6) ease of monitoring. It is anticipated that the sensor could be readily applied to specific bond critical areas of an aircraft to monitor the water ingress to the bondline.

Authors

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Tan Truong completed his Master of Engineering at Tokyo Institute of Technology (Japan) in 1977 and PhD at the University of Adelaide in 1980. He joined DSTO in 1987 and has worked on a number of research and development projects on organic materials for defence applications. He led a group to develop the use of electroactive polymers (EAP) as radar absorbing materials and corrosion protection coatings. He is currently investigating the potential use of EAP for sensors and actuators with applications in surface ship and submarines.

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Christina Olsson-Jacques is a professional officer with DSTO. After completing an Honours degree in Physics at Monash University she commenced employment at the Aeronautical and Maritime Research Laboratory, DSTO in 1990. In 1991 Christina was attached to the Royal Aerospace Establishment DERA Farnborough UK to research residual stress measurements on advanced aircraft alloys. Since returning to AMRL in 1992 her experience has broadened to include adhesive bonding research for through-life support of ADF assets. Recently her research emphasis has moved towards smart materials and sensors for defence applications.

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Sarina Russo is a Technical Officer in the Maritime Platforms Division at AMRL. She joined DSTO in 1981 as a Trainee Technical Officer, completing her studies in 1985, and receiving a Certificate of Applied Science from Footscray College of TAFE. At AMRL her experience includes research and analysis of anechoic tiles used for the Australia's Collins Class Submarine, and providing technical expertise to Conducting Polymer Research. Most recently she has been involved in providing technical support to characterise MHC composite materials to determine their fire hazards and long term properties for Naval Applications.

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Richard Muscat is a professional officer with DSTO. He completed a certificate in Applied Science at Footscray TAFE (1990) and a degree in Applied Science at Victoria University of Technology (1996). He joined DSTO in 1987 and has worked in a number of research and development areas. A large proportion of expertise during this time has been in the spectroscopy areas as a Microanalyst. He has contributed to tasks like electroactive polymers and is currently involved in MEMS task.

Contents

1. Introduction

A number of conventional organic and inorganic materials have been used as sensing materials for humidity [1-8]. Depending on the operating principles, the humidity sensors can be classified into three categories based on (1) the change in electrical resistivity, (2) the change in capacitance and (3) the gravimetric change on absorbing water vapour (eg. a quartz crystal oscillator). A number of polymer-based humidity sensors have been examined by Sakai et al [1-4] and Sata [5]. Metal oxides such as porous thin films of alumina have been used for humidity sensors since the 1940s [9]. Other examples of humidity sensing oxides are SnO_2, TiO_2, Fe_2O_3, MnOx, ZrO_2, ZnO [10] and $MnWO_4$ [11]. Detection of water can be considered as a special case of humidity sensing where the relative humidity is 100% or moisture condenses at a dew point.

The use of conducting polymers as materials for chemical and gas sensors has been widely reported in the literature [12]. In particular, humidity and gas sensors using polypyrrole (PPy) as a sensing material have been described [13-16]. After exposure to a gas or a vapour of volatile substances, the conductivity of conducting polymers can reversibly return to the original value. The reversibility is a main feature for most sensing applications, when conducting polymers are exposed to humidity or bulk water the reactions between water molecules and the polymers lead to an irreversible increase in resistivity (a decrease in conductivity). Unlike gas or organic vapours, water molecules appear to be strongly bound to the PPy backbone and/or react with the associated dopant. At present, the reaction mechanism between PPy and water molecules is not well understood. For most applications, the effect of humidity/water on the conductivity of conducting polymers has been seen as a disadvantage [14]. However, the magnitude of the response to water can be an advantage for those applications in which the arrival of moisture is the information required.

Water ingress leading to debonding of structural components in critical areas of an aircraft is an issue of importance to the structural integrity of that aircraft [17]. Water ingress into a bondline or water condensation at a dew point is a precursor of degradation of the adhesive bond, since water can hydrolyze the epoxy adhesive and provide an environment for corrosion of an aluminium substrate [18]. The effect of moisture on joint durability has been discussed in several review articles [19 - 21]. Early detection of water in the bondline is an important factor in monitoring the health of an adhesively bonded aircraft. Sensitive sensors capable of detecting a low level of water ingress are being developed as a warning device for early attention and maintenance of the aircraft. The use of PPy potentially provides several advantages over the use of conventional alternative humidity sensors. These advantages include: (1) low costs; (2) simple operating principle; (3) simple manufacturing method; (4) long-term stability in an airless environment; (5) sustaining adhesive strength and (6) ease of monitoring. In this study, PPy was examined as a water detecting material embedded in the adhesive and in contact with the aluminium substrate.

2. Experimental

2.1 Preparation of PPy

PPy powder with and without a dopant was manufactured by a chemical method described in a previous report [23] using freshly distilled pyrrole and ferric chloride ($FeCl_3$) as an oxidant. The dopants used in the present study were 5-sulfosalicyclic acid dihydrate (SSA) (Aldrich, 99%) and anthraquinone-2-sulfonic acid sodium salt monohydrate (AQ) (Aldrich, 97%). The powder was compressed into a disc (25 mm ϕ and 1mm thick) under a pressure of 1.5 ton/in² for conductivity measurement. The conductivity was 12 S/cm. For the PPy without a dopant (PPy/0), the conductivity was 2 S/cm.

2.2 Thermal Ageing

2.2.1 "Dry" environment (oven) 50 °C and hot/humid environment (95% humidity 50°C)

The compressed powder was aged at 50 °C on a bed of silica gel in a laboratory oven with a humidity of 7 %. Also, the compressed powder was aged at 50 °C in a desiccator on a saturated solution of potassium sulfate. At 50 °C, this solution gives 95 % humidity. The conductivity was measured with the four-probe technique using potentials recorded with a Datataker 505 (Data Electronics Ltd.).

2.2.2 Airless environment

Fig. 1 shows the structure of the cell where the compressed PPy powder was embedded in the epoxy adhesive (FM 73). A square window of 2mm wide was cut in the middle of the adhesive sheet to accommodate a compressed PPy sample. The adhesive sheet with PPy sample was then sandwiched between two 2024 aluminium substrates (2.5 x 5.0 cm). This adhesive sandwich was cured in a Platen press at a pressure of 60 psi and a temperature of 120 °C for 1 hour. The thickness of the bondline is approximately 0.1 – 0.2 mm. The resistivity of the cell was recorded to ensure good contact between the PPy and aluminium. The resistivity of each cell varies with the size of PPy. The cell was then subject to ageing at 140 °C in a laboratory oven for several months. A second ageing test was also carried out by cycling for several months between a temperature of 100°C for 5 days and room temperature for 2 days.
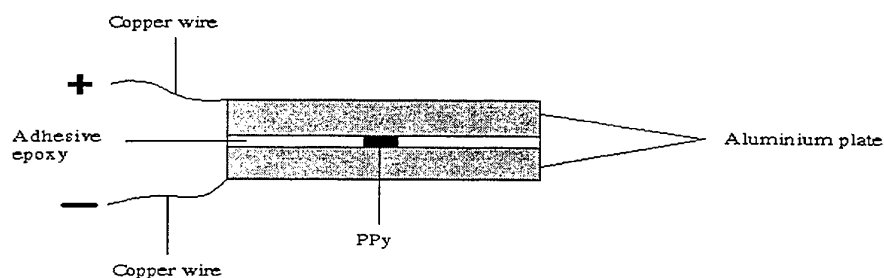
Figure 1:   The structure of a cell with compressed PPy powder

2.3 DC Measurement in water

Fig. 2 shows the sample configuration used for DC measurement. A compressed PPy powder in contact with two flexible copper wires was placed between two adhesive sheets. The sheet sample was cured in the Platen press as described above. The sample was immersed in deionized water. The resistivity was recorded with a multimeter as a function of immersion time.
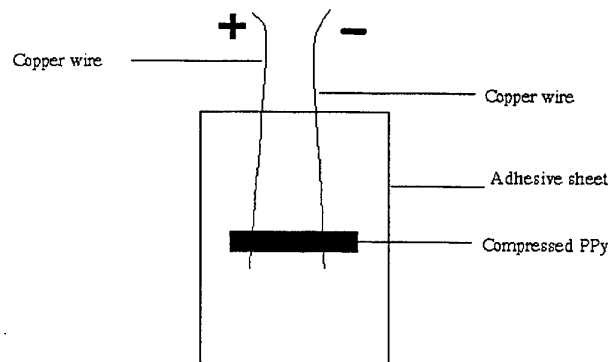

Figure 2:   Sample for DC measurement.

2.4 Impedance and Resistance Measurements

Fig. 3 gives the set up for the resistance and impedance measurements. Leads were connected to the aluminium (2024) cylinders to measure the impedance spectra across the bondline. Impedance spectra were taken using a Hewlett Packard LF Impedance Analyser over the frequency range 10Hz to 10MHz. A digital multimeter was used to measure the DC resistance across the bondline.
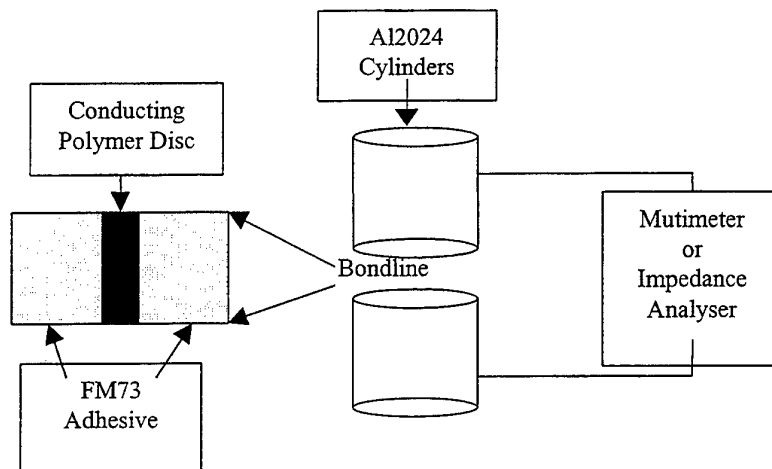

Figure 3a: Set up diagram of impedance and resistance measurements.

2.5 Adhesive Bonded Joints

Two aluminium (2024) 25 mm cylinders were used to manufacture an adhesive bonded joint using FM73 as the epoxy film adhesive. Several adhesive joints were manufactured using one of the two surface preparations given in Table 1. The conducting polymer (CP) discs were inserted at various positions (Fig. 3b) into the adhesive bondline during the placement of the adhesive (lay-up) onto the adherends after surface preparation. The conducting polymer was NSR-2 which has an SSA dopant. The joints were then cured in a Platen press at 120°C for 1 hour. The bondline of the specimens was measured using a Sound Vision CMOS-PRO® 1000 series digital camera connected to a Macintosh Computer. The software used was Adobe PhotoShop® and several measurements were taken around the bondline of each specimen and the results averaged.
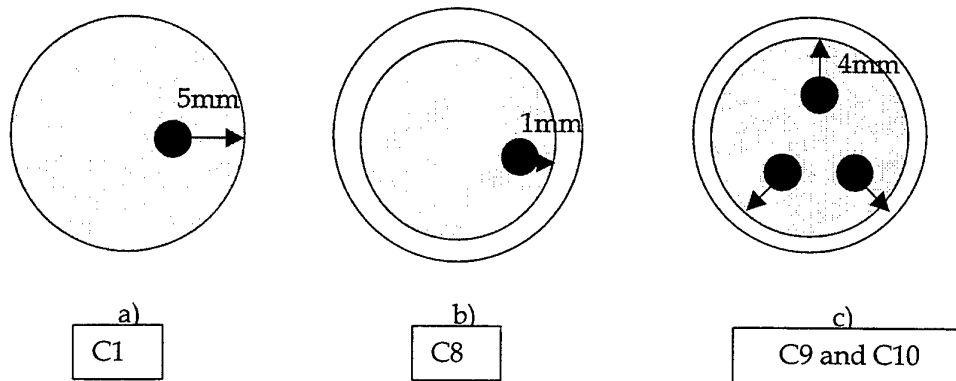
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Figure 3b: Positions of the conducting polymer discs in the adhesive bondline, a) C1 with one disc 5mm from edge of adhesive, b) C8 with one disc 1mm from edge of adhesive, c) C9 and C10 with 3 discs at 4mm from edge of adhesive. (Note that in C8-C10 the adhesive was cut 1mm from edge of adherend to prevent overflow of the adhesive across the bondline).

Table 1: Pre-bond surface preparations and bond cure conditions used for aluminium FM73 joints.

Grit-blast	Grit-blast + Silane
MEK solvent wipe with Kimwipes®	MEK solvent wipe with Kimwipes®
Scotchbrite® abrade	Scotchbrite® abrade
Distilled water wipe with Kimwipes®	Distilled water wipe with Kimwipes®
Dry 100°C for 15 mins	Dry 100°C for 15 mins
Automated Grit-blast	Automated Grit-blast
	Silane 1%aq immersion
	Dry 110°C for 1hr
Bond Cure Conditions.	
Prepare adhesive sandwich with FM73 adhesive and with conducting polymer insert and cure in Platen Press 0.31MPa and 120°C for 1 hour.	Prepare adhesive sandwich with FM73 adhesive and with conducting polymer insert and cure in Platen Press 0.31MPa and 120°C for 1 hour.

A list of the preparation of each adhesive joint is given in Table 2.

Table 2: Adhesive Joints: Preparation details (CP=Conducting Polymer).

No.	Adherend	Adhesive	CP	CP Diam (mm)	CP Mass (g)	CP thickness &/or Bondline – thickness (mm)	CP Position from edge (mm)	Surface prep (Al)	Initial resistance (kohms)	Tests	Comments
Y7	Al2024 25mm diam,	FM73 25mm diam	None			(bondline ~0.1mm)		Grit-blast +Silane		0.001M NaCl	Control
Y20	Al2024 25mm diam,	FM73 25mm diam	None			(bondline ~0.1mm)		Grit-blast		Instron Adhes. Strength	
Y5	Al2024 25mm diam,	FM73 25mm diam	None			(bondline ~0.1mm)		Grit-blast +Silane		Instron Adhes. Strength	
J1	Al2024 25mm diam,	FM73 25mm diam	None			(bondline ~0.1mm)		Grit-blast		Instron Adhes. Strength	
J7	Al2024 25mm diam,	FM73 25mm diam	None			(bondline ~0.1mm)		Grit-blast +Silane		Instron Adhes. Strength	
C1	Al2024 25mm diam,	FM73 25mm diam	NSR-2	5mm	0.0042g	0.2-0.3 mm (bondline= 0.3)	5mm	Grit-blast	Open Circuit	Instron Adhes. Strength	CP not contacting Al
C8	Al2024 25mm diam,	FM73 *24mm diam	NSR-2	5mm	0.010 g	0.403 mm (bondline= 0.43)	1mm	Gritblast	0.017	0.001M NaCl	
C9	Al2024 25mm diam,	FM73 *24mm diam	NSR-2	5mm	0.011 0.011 0.011	0.439 0.451 0.452 (bondline= 0.46)	4mm (3 discs)	Grtiblast+ Silane	0.021	0.001M NaCl	Relatively low resistance could be due to having 3 discs = greater contact area.
C10	Al2024 25mm diam,	FM73 *2mm diam	NSR-2	5mm	0.012 0.012 0.013	0.478 0.486 0.503 (bondline= 0.49)	4mm (3 discs)	Gritblast	0.004	0.001M NaCl	Relatively low resistance could be due to having 3 disc and thicker discs=> contact increased with Al

2.6 Adhesive Strength Studies.

Four "standard" specimens without conducting polymer discs were selected for adhesive strength tests. One specimen with a conducting polymer disc was selected for testing to consider whether the inclusion of the conducting polymer disc in the bond line degraded the adhesive bond strength. The specimens were tensile loaded to failure in a 100kN Instron static testing machine. The tests were carried at a speed of 0.5 mm/min and the failure load taken from the chart recording.

2.7 Water Ingress Studies with immersion of the adhesive joints in 0.001M NaCl solution.

The adhesive joint specimens were immersed in 0.001 M NaCl solution at room temperature consistent with the ionic concentration in tap water. The specimens were removed from solution, dried with Kimwipes® and then under a hair dryer for 30 seconds to remove excess water across the bondline. Specimens were allowed to cool for at least 5 minutes prior to measurements. Impedance spectra were taken at periodic intervals to monitor changes in impedance due to the ingress of water into the bondline. Specimens were re-immersed in the 0.001M NaCl solution after the measurements.

3. Results and Discussion

3.1 Thermal Ageing:

3.1.1 At 50°C ("Dry" & Humid Environments)

The oxidative degradation of PPy at 50°C in a "dry" oven (7 % humidity) and at 95 % humidity is shown in Fig. 4. The degradation results in a rapid increase in resistance. In Fig. 4, the increase in resistance is expressed by $(R - R_0)/R$ where R_0 is the initial resistance and R is the resistance at time t. The order of increase in resistance both in a "dry" environment and 95 % humidity is as follows: PPy/0 > PPy/SSA >PPy/AQ. Obviously, the specific nature of dopant greatly affects the degradation of the PPy backbone. Moisture exacerbates the increase in resistance for all samples. The effect of moisture can be clearly observed for the case of PPy/AQ powder. The resistance of this sample remained unchanged at 50C in the oven, while an increase of 50% of the initial resistance was observed after 280hours of ageing at 50°C/ 95% humidity.

It should be noted that the resistance initially decreases before increasing (indicated by the values of $(R - R_0)/ R$). This dramatic decrease is caused by both thermal annealing observed for PPy in dry environments [24, 25]. A similar decrease in resistance was also observed in PPy coated poly(ethylene terephthalate) when the environment changes from dry air to 14 % humidity [14].
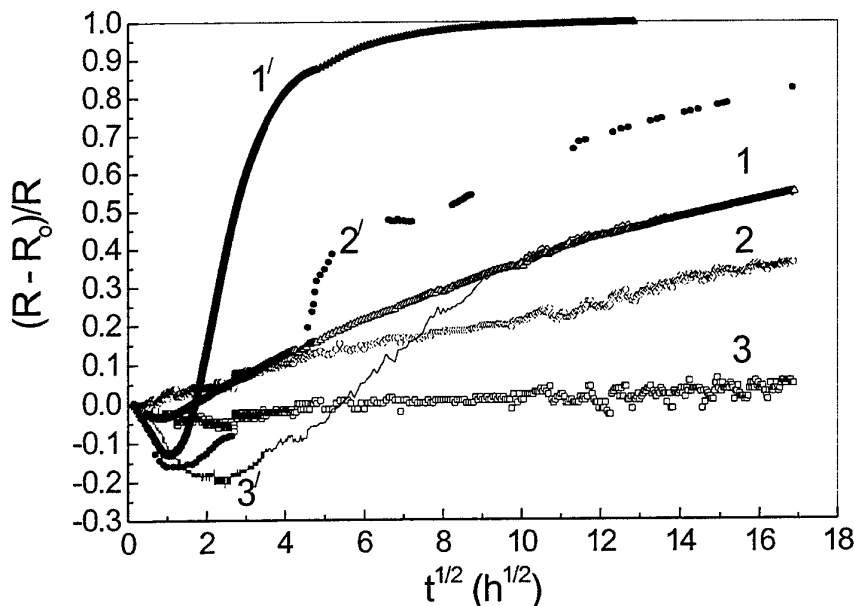
Figure 4: *Resistivity increase by oxidative degradation of PPy powder at 50C . In a "dry" environment (7 % humidity): (1) PPy/0; (2) PPy/SSA and (3) PPy/AQ. In an environment of 95 % humidity: (1') PPy/0; (2') PPy/SSA and (3') PPy/AQ*

The water molecules also contributed to the initial decrease in resistance [14]. The initial decrease in resistance shown in Fig 4 is likely attributed to polarization of electronic charge of the adsorbed water molecules resulting in additional free hole charge carriers which cause an increase in conductivity and thus a decrease in reistivity [14]. Further absorption water causes swelling which may block the electronic pathway and thus an increase in resistivity is observed as a result. As mentioned in a later section, swelling is the main factor affecting conductivity decay (increase in resistivity) when PPy powder contact with water.

3.1.2 Airless Environment

Thermal ageing in air (70 – 150°C) caused by oxidation has been examined on PPy doped with different dopants [23, 26]. It has been confirmed that oxygen can attack both the PPy backbone and the dopant [27]. Since the specific molecular properties of the dopant profoundly affect the degradation kinetics of PPy, it has been found that when AQ is incorporated to PPy as a dopant, the resultant PPy/AQ powder shows excellent resistance to thermo-oxidative degradation [23]. In the airless environment (Fig. 1), the PPy powders are thermally stable. For example, the resistance R of the

compressed PPy/SSA powder remained unchanged nearly 2000 h at 100°C (Fig. 5). During the test, the cell was taken out of the oven periodically to cool down to room temperature overnight. As a result, the R value increased to 300 – 400 Ω at room temperature and dropped back to a similar value at 100°C. It should be noted that the resistance of a conducting polymer decreases with increasing temperature [28]. The R value at room temperature can be considered as a baseline value to confirm the thermal stability of the powder. The PPy/AQ powder also showed similar stability under the same testing conditions.
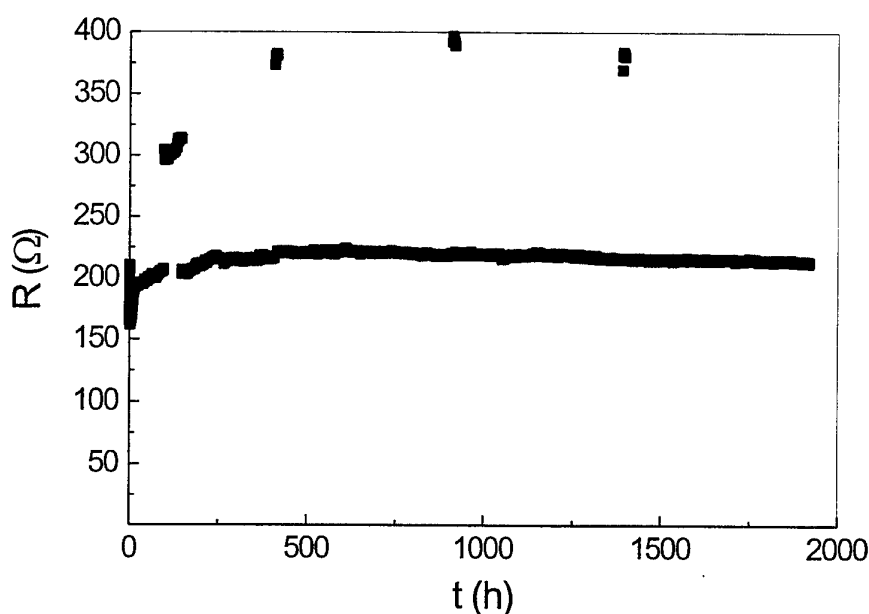

Figure 5:   *Resistivity of a compressed PPy/SSA powder embedded in the bondline and aged at 100 °C*

Fig. 6 shows the R value of PPy/0 respond to the temperature changed between room temperature and 100°C. The R value at 100°C is lower than that at room temperature. Switching between room temperature and 100ºC mimics the changing climatic conditions in a real situation. The R value is almost unchanged at each constant temperature. In particular, the R value is stable at 100°C, given the PPy/0 sample exhibiting rapid degradation in the presence of oxygen (Fig. 4). It has been known that since PPy/0 was synthesized without incorporating a dopant, the material is very vulnerable to thermo-oxidative decay [23]. However, the data shown in Fig. 6 again

confirm that in the airless environment PPy is thermally stable, even though the material can decay rapidly in air.
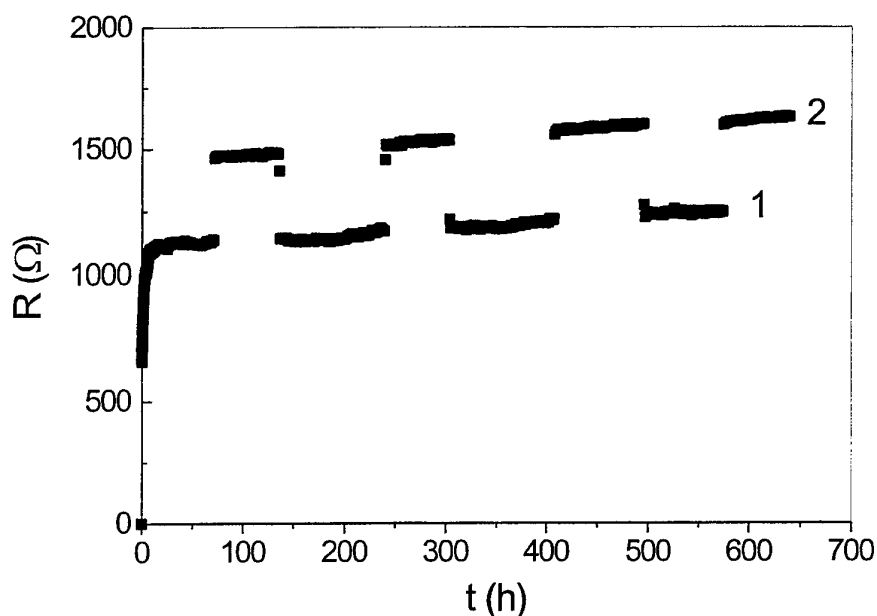

Figure 6: *Resistivity of a compressed PPy/0 powder embedded in the bondline aged at temperatures alternatively switched between (1) 100 °C and (2) room temperature.*

3.2 DC and AC Measurements

3.2.1 DC Resistivity

Fig. 7 shows a dramatic increase in DC resistance, R, when the PPy is in contact with water diffusing through the epoxy coating. The porous nature of the PPy powder facilitates high absorption of water. The increase in R results from swelling the PPy network with water which blocks the electronic conducting path. In contrast to moisture absorption, the initial decrease in R (Fig. 4) was not observed in bulk water absorption. This indicates the swelling occurs immediately. The R values increase linearly with time t initially before a higher increase rate was observed at the later stage. Obviously, the increase in R does not follow the diffusion rate of water by Fickian diffusion kinetics. In practical applications, the rapid increase in R as the PPy

"sees" the bulk water is a desirable property as a sensor. Similar results were also observed in brine solutions.
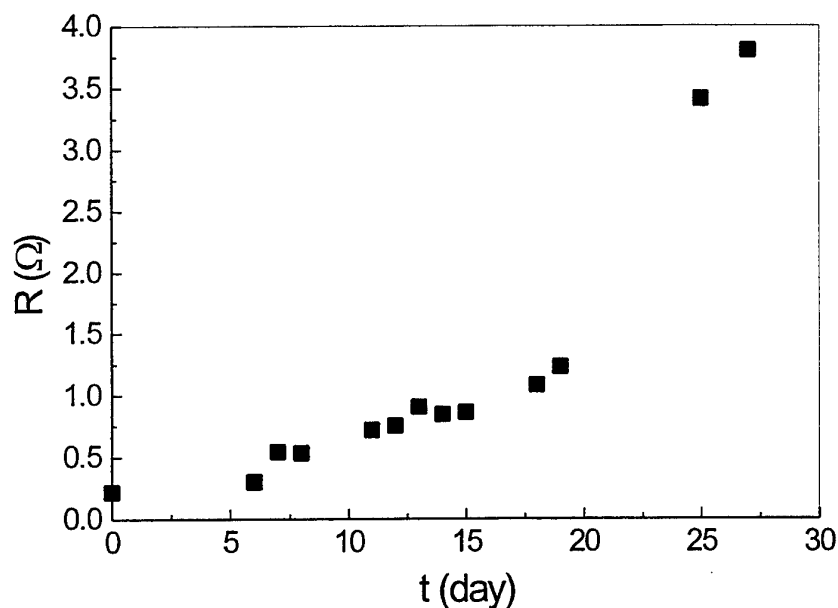

Figure 7:   *Increase in resistance R in contact with water of PPy powder.*

3.2.2 Impedance Spectroscopy

Fig. 8 shows the variation of the bond line impedance without PPy. At low frequencies, the impedance is equivalent to the resistivity. The overall impedance decreases with increasing immersion time. The decrease, which is significant at low frequencies, indicates a large decrease in the resistance R of the bond line (from the order of 10^6 to 10^4 Ω in 3291 h immersion) due to water absorption. On the other hand, for the bondline with PPy the impedance increases with increasing time (Fig. 9). For example, the R value increases from the order of 10^3 to 10^4 Ω in 1010 h immersion in a sample with a PPy disc in the centre, from 10^1 to 10^3 Ω in 1032 h immersion a sample with three PPy discs (Fig. 10).

At a first approximation, any capacitance effects can be ignored in the impedance data at low frequencies. It can be postulated that the resistance of the adhesive R_a, water absorbed adhesive R_{wa} and PPy R_{PPy} are connected in parallel as shown in the circuit below. The current flows mostly through the lowest resistance. In the absence of PPy,

R_{wa} is much lower than R_a due to water absorption. As more water is absorbed in the adhesive, the R_{wa} decreases. In the presence of PPy, R_{PPy} is the smallest resistance of the overall circuit. The absorption of water to PPy results in an increase in resistance due to swelling in the PPy networks blocking the electronic conductive pathways. Therefore, during water ingress two opposite factors, i.e. decreasing R_{wa} and increasing R_{PPy}, contribute to the change of the impedance at low frequencies. However, since R_{PPy} is initially several decades lower than R_{wa}, the overall impedance is still dependent on the increasing R_{PPy} with immersion time.
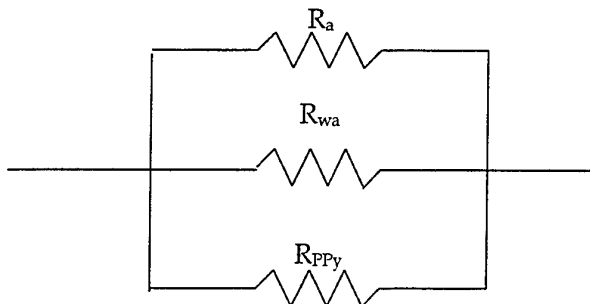
The shape of the impedance in the medium to high frequencies (10^3 to 10^7 Hz) is dependent on the resistances and capacitances. Due to the complexity of the sample configuration, however, establishing an equivalent circuit is beyond the scope of this study.

It has been previously found that the non-conducting polymer impedance spectroscopy could be modelled using a modified version of the electrode circuit model given in references [29 - 30]. The dry adhesive joint was represented by the capacitance C_a, while R_w represents the leakage resistance as the ionised water ingresses into the adhesive and Z is an impedance component representing the electrical characteristics of the bond interface (typically given as a parallel RC circuit). For the addition of the polypyrrole discs we can add a resistance in parallel to this circuit R_{PPy} as given in the figure below. In the case of the non-conducting polymer (Fig. 8) the 0 h measurement is dominated by the capacitive term C_a, however as the water ingresses the R_w and Z terms influence the impedance and phase plots. In the case where there is a conducting polymer disc (Figs. 9 and 10) the R_{PPy} term dominates. There is more complex behaviour occurring with water ingress into the bondline during the environmental exposure particularly at high frequencies.

In the conducting polymer case the most useful frequencies that could be used to measure the change in disc with water ingress are the lower frequencies eg. 10Hz. However as the R_{PPy} term dominates over the terms due to the water ingress into the adhesive it could be much simpler to measure the change in this resistance using a multimeter for in-field applications.
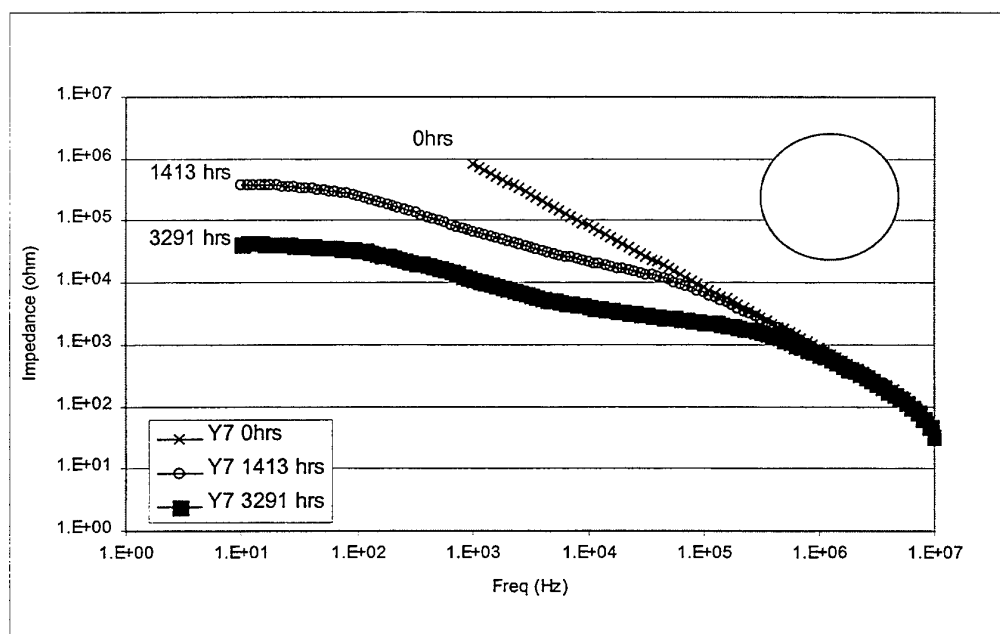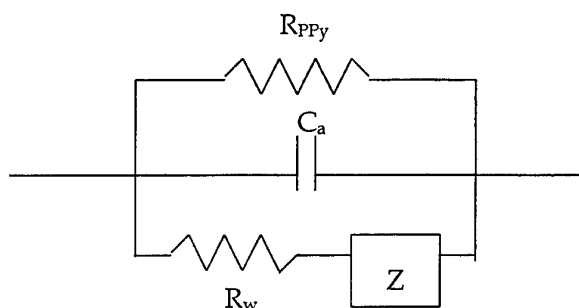
Figure 8a: Impedance plot across the bondline without PPy immersed in 0.001 M NaCl solution (sample Y7).
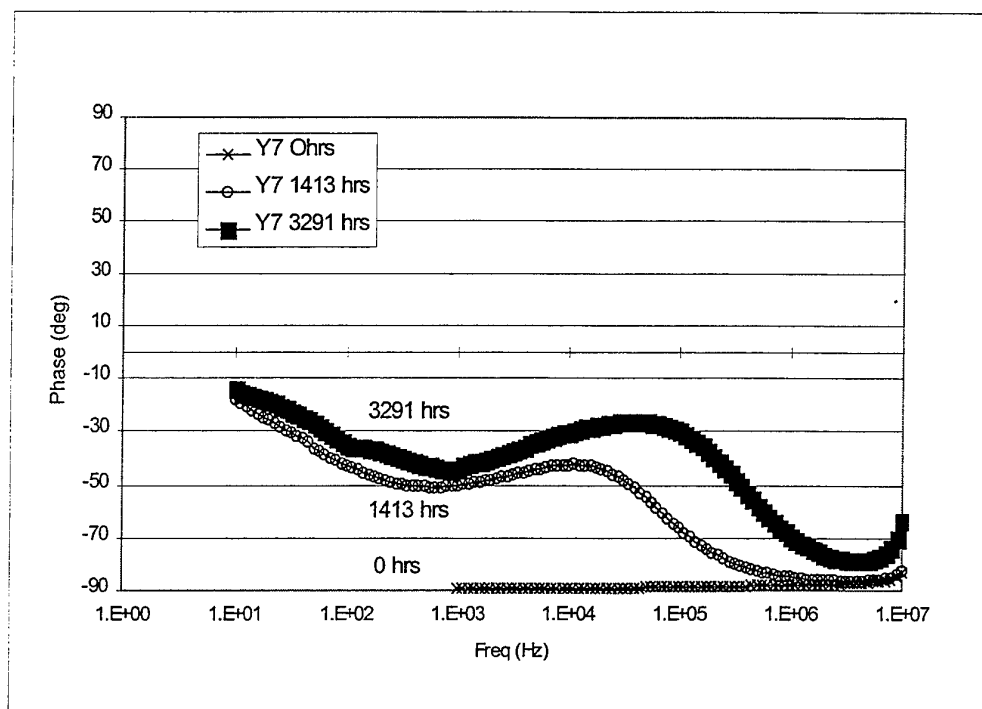
Figure 8b: *Phase plot across the bondline without PPy immersed in 0.001 M NaCl solution (sample Y7).*
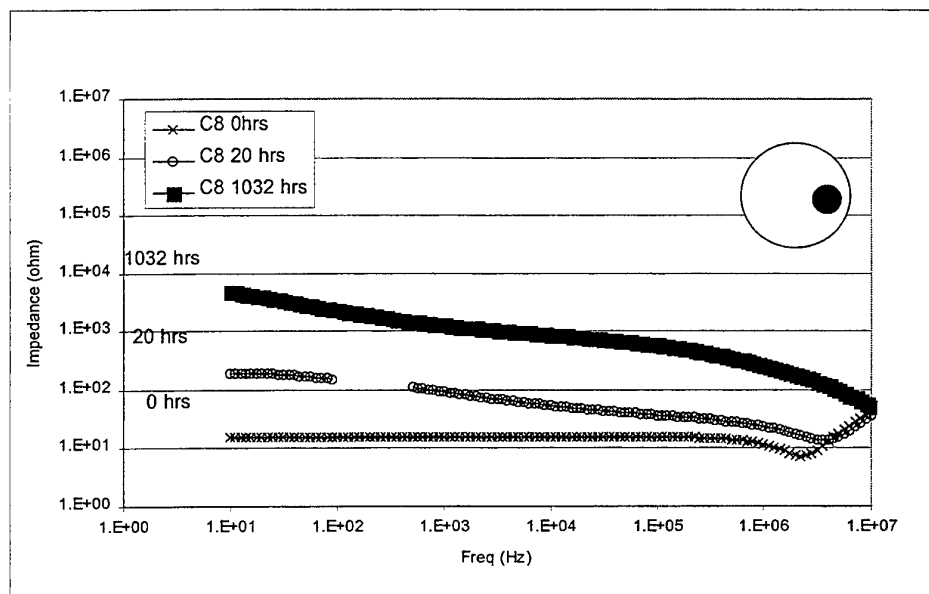
Figure 9a: Impedance plot across the bondline with one PPy disc (5 mm diameter) immersed in 0.001 M NaCl solution (sample C8).

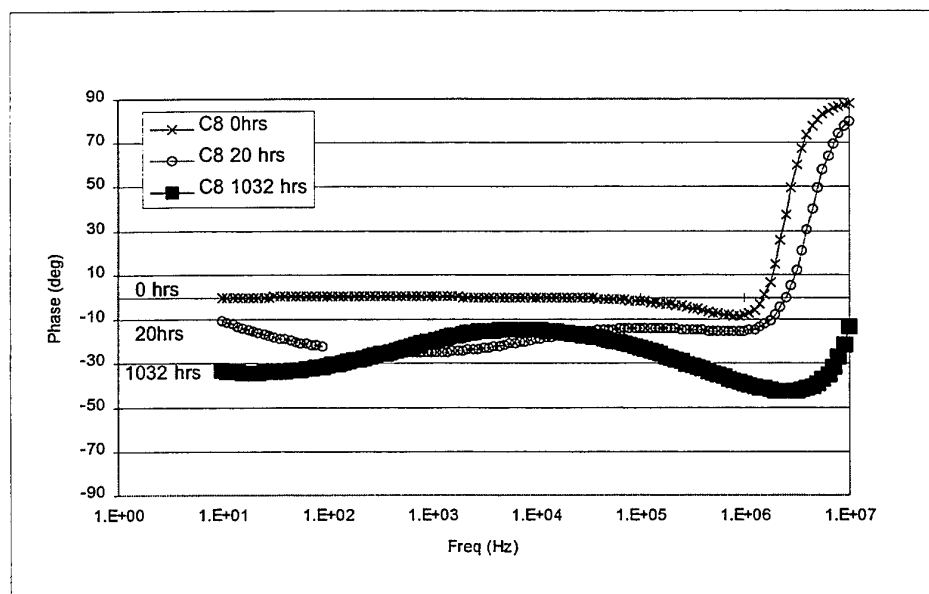*Figure 9b: Phase plot across the bondline with one PPy disc (5 mm diameter) immersed in 0.001 M NaCl solution (sample C8).*
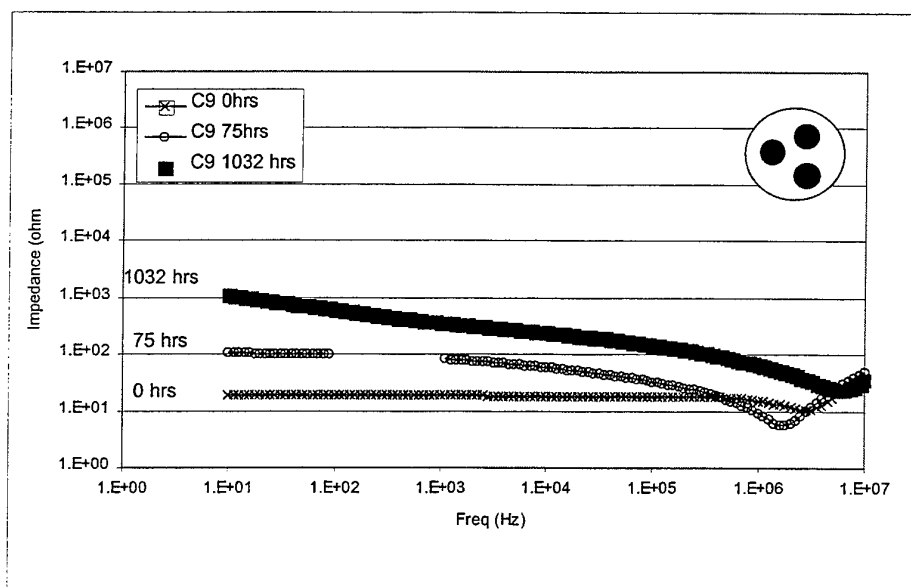
Figure 10a: Impedance plot across the bondline with three PPy discs (5 mm diameter) immersed in 0.001 M NaCl solution (sample C9).
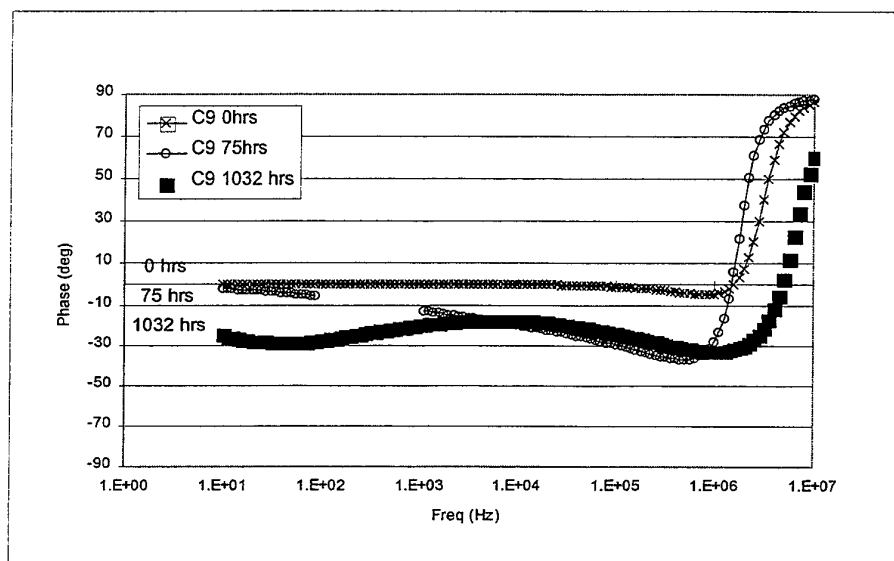

Figure 10b: Phase plot across the bondline with three PPy disc (5 mm diameter) immersed in 0.001 M NaCl solution (sample C9).

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3.3 Adhesive Strength

3.3.1 Dry Adhesive Strength

The results from the dry strength Instron testing are given Table 3. The failure load of 23.5 kN for the specimen with PPy (C1) was consistent with other failure loads in specimens without the conducting polymer disc (i.e. 23.8 kN and 23.1kN). The failure surface of specimen C1 is given Fig. 11. In general the adhesive appears to have failed cohesively except at the edge where the conducting polymer disc was positioned. This may be due to the 0.3 mm disc increasing the bondline thickness (typically 0.1 mm thick) in this region. From Table 3, it has been confirmed that the inclusion of the conducting polymer disc of thickness 0.3 mm did not significantly decrease the dry adhesive strength of the adhesive joint.

Table 3: Dry Adhesive Strength Tests.

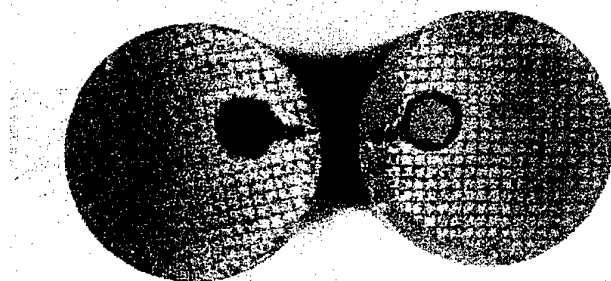| Specimen	Surface Preparation	Failure Load (kN)
Y20	Grit-blast	23.8
J1	Grit-blast	23.1
C1	Grit-blast (with PPy)	23.5
Y5	Grit-blast+ Silane	25.3
J7	Grit-blast + Silane	25.6

Figure 11:   Failure surfaces of C1 loaded to failure in a 100 kN Instron machine

3.3.2 Wet Adhesive Strength

Specimen C10 fell apart (adhesive strength = zero) in the 0.001M NaCl solution after ~800hrs immersion. The failure surface is given in Fig. 12. There appears to be adhesional failure of the aluminium to adhesive. There is also conducting polymer on both failure surfaces indicating that the disc had failed internally. The inclusion of three relatively thick PPy discs in the bondline may have contributed to an easier path for ingress of water into the bondline leading to premature failure compared to the other adhesive joints. Further studies should be undertaken to optimise the thickness and percentage surface area of the PPy discs in the adhesive bondline.
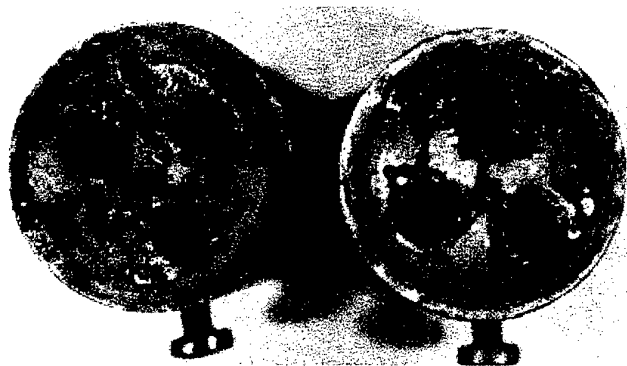

Figure 12:   Failure surface of C10 after ~800 h immersion in 0.001M NaCl. Note the adhesive strength was zero and the specimen fell apart in solution.
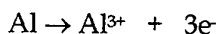
3.4 Design of a Sensor with PPy

Inclusion of PPy in the adhesive bondline provides a simple sensor for detecting water ingress. The following important requirements for a successful operation in a real situation are: (a) acceptable bond strength, (b) sensitivity to water (c) ease of monitoring and (d) thermal stability. As shown in the previous section, inclusion of a PPy disc of 5 mm in diameter in a bonded joint of 25 mm diameter does not reduce the adhesive strength. The DC resistivity increases rapidly when the PPy is in contact with water. This is consistent with the impedance obtained by AC measurements at low frequencies that show an increase in R_{PPy} and a decrease in R_{wa} and clearly indicate that the increase in R_{PPy} is the dominant factor (Figs. 9 and 10). The agreement between the DC and AC (low frequencies) results justifies the use of a simple device (eg. a multimeter) to monitor the resistivity during water ingress. It should be noted that resistance of the PPy increases in contact with water and does not come back to the
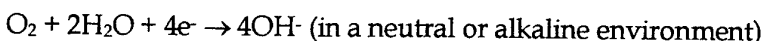
initial value even when the PPy is dried [31]. The reasons for this irreversible increase in the resistance by water remain unclear.

If the corrosion process ensues in the bondline due to water ingress, the anodic and cathodic reactions can be express by
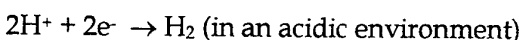
Anodic reaction:
$$Al \rightarrow Al^{3+} + 3e^-$$

Cathodic:
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (in a neutral or alkaline environment)}$$
or
$$2H^+ + 2e^- \rightarrow H_2 \text{ (in an acidic environment)}$$

The production of the hydroxyl ion OH^- changes the pH of the corrosion environment. The ion can undergo ion exchange with the dopant of the PPy or attack the PPy backbone leading to a rapid and substantial increase in resistivity. This is an irreversible process. For example, a concentration of $10^{-3} - 10^{-4}$ M of OH^- can increase the resistivity by a factor of 100 in few minutes [27]. Therefore, in addition to the increase by water the resistivity can further increase as the corrosion proceeds. Furthermore, the formation of a non-conductive passive oxide layer [32] on the aluminium surface in the corrosion process can produce an increase in charge transfer resistance at the contact between PPy and the aluminium substrate.

Bond cure temperatures of epoxy adhesives used in aircraft are typically up to 200°C. The adhesives used in this study were cured at 120°C. However, degradation of PPy during curing of the adhesive is minimal owing to the good thermal stability exhibited in an airless environment. Thermal stability of the PPy is an important factor in service once the material is included in the bondline of an aircraft. It has been found in a previous study [23] that SSA or AQ as a dopant provided a good resistance against thermo-oxidative degradation. The present study demonstrates that the PPy/SSA and PPy/AQ powders exhibit a good stability at 100°C in an airless environment for at least 2000 h (Fig. 5). On the basis of this study, PPy powder can be considered as a candidate material for moisture detecting in aircraft bondline. However, prior to full implementation to a real situation, the following tests should be performed:

(1) The performance and thermal stability of PPy will be performed with time at operating temperatures (-50°C to 50°C) of the aircraft.
(2) The PPy should be thermally/environmentally stable in the entire service time of an aircraft. Accelerating ageing tests and long-term field tests should be performed to ensure the life span of encapsulated PPy in service.
(3) The aluminium substrate expands and shrinks in the range -50 to 50°C. The contact between the PPy and aluminium substrate may be loosened as a result causing an increase in resistivity which can be mistaken as decay due to thermal degradation. Although this can be a concern in reality, a conducting mixture of adhesive and PPy

powder can be used instead of compressed PPy to increase the adhesion strength at contact areas.

4. Conclusion

The PPy of this study exhibited good thermal stability in when embedded in epoxy adhesive. On doping the PPy with SSA or AQ, the dopant further enhances the thermal stability. The inclusion of PPy in the adhesive of the bondline provides a simple sensing configuration to detect the water ingress. Swelling of PPy results in a rapid increase in resistivity which can be detected by DC measurements and impedance spectroscopy. The consistency between the DC resistivity and the impedance at low frequencies justifies the use of a multimeter for on-site monitoring. In the laboratory tests, the PPy met the requirements on (1) sensitivity to water ingress, (2) thermal stability and (3) sustaining the dry adhesive strength. Although the resistance of the PPy in the bondline was unchanged at 100°C for at least 2000 h, further study should be conducted in on-site environments or accelerated ageing test to ensure the thermal stability in a real situation.

The water ingress irreveribly increases the resistance of the PPy and will eventually lead to corrosion resulting in the change of pH at the cathodic reaction due to hydroxyl ion. The reactions between the PPy and hydroxyl ion and the formation on non-conductive aluminium oxides will further increase the resistivity.

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19. ABSTRACT

A simple and low cost sensor for detecting the water ingress in the adhesive bond line was designed. A compressed polypyrrole (PPy) powder was embedded in an epoxy adhesive sandwiched between two aluminium (2024) substrates. Interactions between PPy and water resulted in a rapid increase in resistivity. The DC resistivity increased more than 20 times the initial value when the PPy was contacted by water. The increase was consistent with AC impedance at low frequencies which showed 10 times increase if one PPy disc (3 mm diameter) was embedded or 100 times increase if there were 3 PPy disc embedded when the cell was immersed in a brine solution for approximately 1000 h. The resistivity of compressed PPy embedded in the bondline was unchanged after 2000 h ageing at 100 C. This indicates a good thermal stability. An initial test indicated that the inclusion of a single 5mm diameter PPy disc in a 25mm diameter bonded joint did not significantly decrease the dry adhesive strength of the adhesive joint. These results indicate that the sensor could potentially meet the requirements of a bond degradation sensor in terms of (1) low cost (few cents for one PPy disc) (2) sensitivity to water (3) long-term stability (4) ease of monitoring and (5) sustaining the dry bond strength.